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Development of Room Temperature Ionic Liquids for Applications in Actinide Chemistry

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One area of on-going research in our group at Los Alamos National Laboratory is directed toward characterization of the basic coordination chemistry and electrochemical behavior of f-element ions dissolved in room temperature ionic liquids (RTILs). The ultimate goal of this work is to introduce advanced, environmentally sustainable, nuclear processing and purification strategies into both the DOE complex and the civilian nuclear industry. Efforts to develop ambient temperature electrorefining and/or electrowinning technologies are focused on the design of ionic liquids characterized by extended cathodic stability. In this chapter a summary of the synthesis, physical properties and electrochemical behavior of the ionic liquids used in this work is presented. The feasibility of efficient electrochemical production of high electropositive metals is demonstrated through reversible plating and stripping of sodium and potassium metals.

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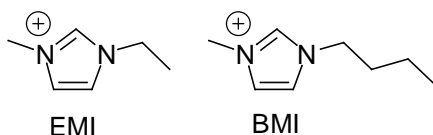
Introduction

The application of room temperature ionic liquids (RTILs) as rationally designed solvent systems to solve chemical and materials science problems is currently attracting a great deal of interest (1). Ionic liquids are low melting organic salts that offer a unique combination of physical properties that can be exploited to develop advanced, environmentally sustainable, chemical technologies. These systems are being actively considered in the development of clean technologies in chemical synthesis, catalysis, electrochemical production of pure metals and alloys, and in chemical separations. A general program has been initiated at Los Alamos National Laboratory to characterize the basic coordination chemistry and electrochemical properties of lanthanide and actinide ions dissolved in RTILs. The goal of this work is to develop advanced, environmentally sustainable, nuclear processing and purification technologies to be implemented within both the DOE complex and the civilian nuclear industry.

Current state of the art in routine actinide recovery and purification can be divided into two main categories: 1) aqueous processing based on PUREX or similar extraction technologies, and 2) electrochemical pyro-refining of metals from high temperature molten salt media (2). In the first category, efficient actinide purification is built upon detailed understanding of the coordination chemistry, hydrolytic behavior, and valence state control of f-element ions and complexes dissolved in aqueous solutions. In the second case, high temperature molten salt electrorefining is used to produce pure actinide metals because of the highly electropositive nature of the metallic f-elements. The actinide metals generally react rapidly and in some cases violently with water to evolve hydrogen and give metal oxides. In order to obtain the pure metals, anhydrous molten salt processes have been developed, which closely resembles the high temperature electrochemical techniques used to produce aluminum metal. Alternative approaches based on RTILs could help solve several long-standing concerns with current technology including nonproliferation issues, criticality safety, equipment degradation, and lack of process flexibility.

Room temperature ionic liquids are fascinating solvents to consider in actinide electrorefining. Development of an RTIL based process to produce pure actinide metals is an attractive possibility. The lower operating temperatures and less corrosive RTIL environment promise reduced production costs. Spent reaction mixtures/solvent systems could be integrated with ion-exchange chromatographic techniques to allow simple recycle schemes that minimize waste. Furthermore, compared to high temperature molten salt conditions, ambient temperature electrochemical processes can be more easily integrated with real-time spectroscopic analysis to allow fine control over reaction conditions and processing parameters. From a safety standpoint the ionic liquids are attractive because they are non-flammable and have essentially no vapor pressure at ambient temperatures. Criticality safety in ionic liquids is also much improved over aqueous solvent systems (3).

The actinides, aside from being notoriously radioactive, are also among the most electropositive elements. The standard reduction potential of thorium, uranium, neptunium, plutonium, and americium are all more negative than aluminum. The reduction potential of trivalent americium compares most closely to that of magnesium. However, the most well-developed and extensively utilized ionic liquids based on 1,3-dialkylimidazolium cations are incompatible with electrochemical actinide reduction. In order for RTILs to be of general utility in actinide electrorefining/electrowinning, the cathodic stability of the solvent must be extended beyond the limits of 1,3-dialkylimidazolium salts (*c.f.* EMI or BMI). Any attempt to reduce f-element ions to pure metals or



alloys in these media would irreversibly decompose the ionic liquid solvent through reduction of the imidazolium ring. In this chapter we summarize our work toward development of RTIL systems characterized by extended cathodic stability. Low viscosity, high conductivity ionic liquids are described and their electrochemical windows are demonstrated. Details of the chemical and electrochemical behavior of actinide ions dissolved in these solvent systems will be reported elsewhere.

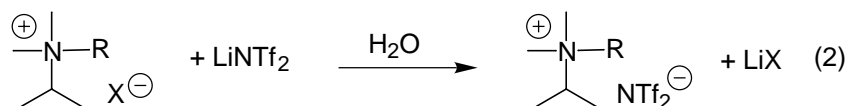
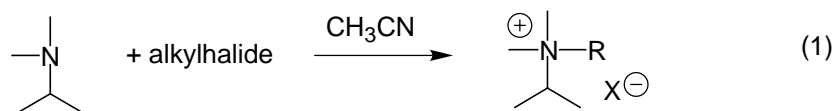
Synthesis and Physical Properties of Ionic Liquids

The physical properties of ionic liquid solvents, such as melting point, density, viscosity, conductivity, and polarity depend upon the chemical structure of both the anion and cation. Detailed studies of 1,3-dialkylimidazolium salts combined with a variety of different anions have shown that bis(trifluoromethanesulfonyl)amide, $\text{N}(\text{SO}_2\text{CF}_3)_2$ (NTf_2), gives air and water stable materials generally characterized by the lowest melting points, lowest viscosities, and highest conductivities of currently available ionic liquids (4). These properties, combined with excellent thermal and electrochemical stability, advocates their use in further ionic liquid development and are exclusively considered in this work.

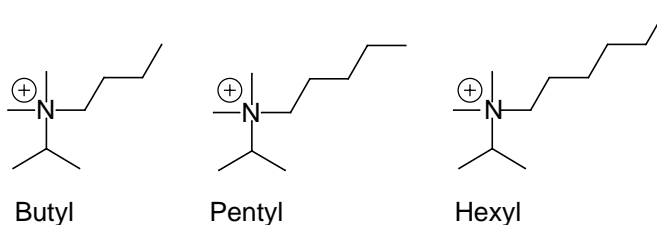
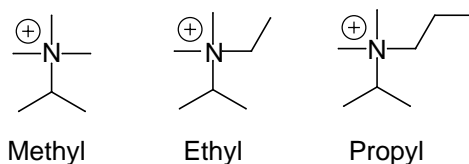
Ionic liquids characterized by extended cathodic stability can be prepared using quaternary ammonium cations. The viscosity of these systems depends markedly on the molecular weight/molecular volume of the cation. For example, while $[\text{N}(\text{Et})_3(n\text{-hex})]\text{NTf}_2$ and $[\text{N}(\text{butyl})_3(n\text{-hex})]\text{NTf}_2$ are each ambient temperature liquids, their viscosity is unacceptable for convenient use as a free flowing solvent (viscosity equals 167 and 595 cP, respectively) (5). It should be emphasized that solvent viscosity is an important property to minimize because rate of solute dissolution, reaction kinetics, ease of handling, and electrical

conductivity can all be optimized using low viscosity ionic liquids. For comparison, the lowest viscosity of currently reported ionic liquids is 34 cP (25 °C) for [1,3-ethylmethylimidazolium]NTf₂ ([EMI]NTf₂), which is only slightly greater than the viscosity of ethylene glycol. These values can be further placed into perspective by recognizing that water has a viscosity of only *ca.* 1.0 cP at ambient temperature.

To address this issue, smaller quaternary ammonium salts have been prepared. A series of [NMe₂(*i*-Pr)(R)]NTf₂ salts have been synthesized and their properties correlated with the alkyl group, R (R = Me, Et, *n*-Pr, *n*-butyl, *n*-pentyl, and *n*-hexyl) (6). A simple aqueous metathesis reaction between a quaternary ammonium halide and commercially available LiNTf₂ gives the corresponding hydrophobic ammonium NTf₂ salt, which generally forms a second liquid layer below the aqueous phase (eqn. 1 and 2). A common work-up

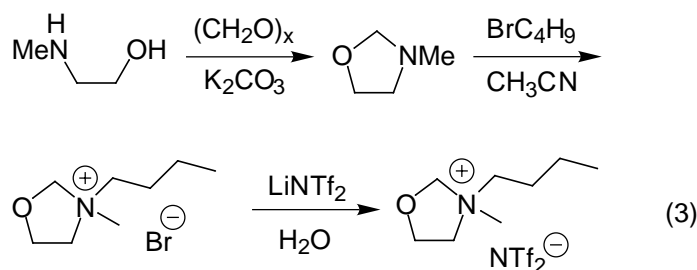


is followed for all the ionic liquids described in this work. Simply decanting the water and repeated extraction with additional aliquots of water removes lithium halide from the crude ionic liquid. The ionic liquids are then dried under vacuum for at least 48 hours, then passed through a column of dry activated alumina to yield colorless, analytically pure, anhydrous solvents. The highest symmetry ammonium salt of the series, [NMe₃(*i*-Pr)]NTf₂, is obtained as a typical ionic

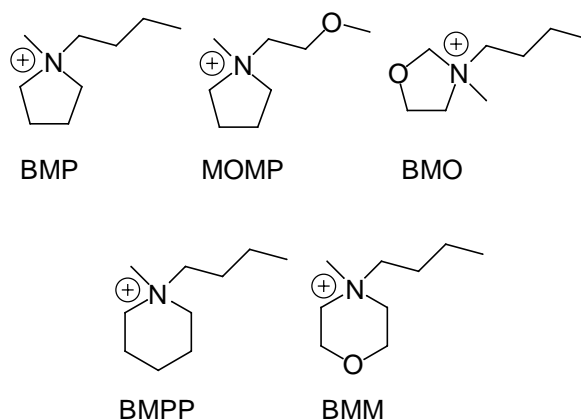


solid (mp = 150 °C) and is isolated by filtration and washed with water. Reduction of the cation symmetry by exchange of one methyl group for an ethyl group (i.e. [NMe₂(Et)(*i*-Pr)]NTf₂), again gives an ionic solid, although the melting point is reduced to 56 °C. When the variable group, R reaches *n*-propyl or larger, ambient temperature ionic liquids are obtained, in which the viscosity gradually increases across the series (*vide infra*).

A promising ionic liquid design strategy has recently been introduced by MacFarlane and co-workers (7). Incorporation of a quaternary nitrogen center into a five-member cyclic structure gives ionic liquids of considerably reduced viscosity compared to acyclic ammonium salts of similar molecular weight. A nice example is illustrated by [N,N-butylmethylpyrrolidinium]NTf₂ ([BMP]NTf₂). When measured at 30 °C, the viscosity of [BMP]NTf₂ is found to be 60 cP, compared to an acyclic ammonium salt of similar molecular weight, [NMe₂(*i*-Pr)(*n*-butyl)]NTf₂, which is characterized by a viscosity of 103 cP.



We have prepared the corresponding [N,N-butylmethyloxazolium]NTf₂ ([BMO]NTf₂) ionic liquid to evaluate the effect of oxygen incorporation into the five-member ring (eqn 3). The viscosity of [BMO]NTf₂ (vis = 108 cp, 30 °C) is found to be considerably larger than [BMP]NTf₂. A similar trend is observed for the corresponding six-member ring cations. Thus, [N,N-butylmethyl-



piperdinium]NTf₂ ([BMPP]NTf₂) is isolated as a relatively viscous liquid while the related [N,N-butylmethylmorpholinium]NTf₂ ([BMM]NTf₂) salt occurs as a low melting (mp = 34 °C) solid. Curiously, we find that substitution of the butyl group in [BMP]NTf₂ with methoxyethyl- significantly reduces the viscosity of the resulting [N,N-(methoxyethyl)methylpyrrolidinium] salt (MOMP; vis = 42 cP, 30 °C). In fact, this salt is characterized by one of the lowest viscosities of any non-imidazolium based ionic liquid. The viscosity and conductance of some of these ionic liquids are summarized in Figure 1.

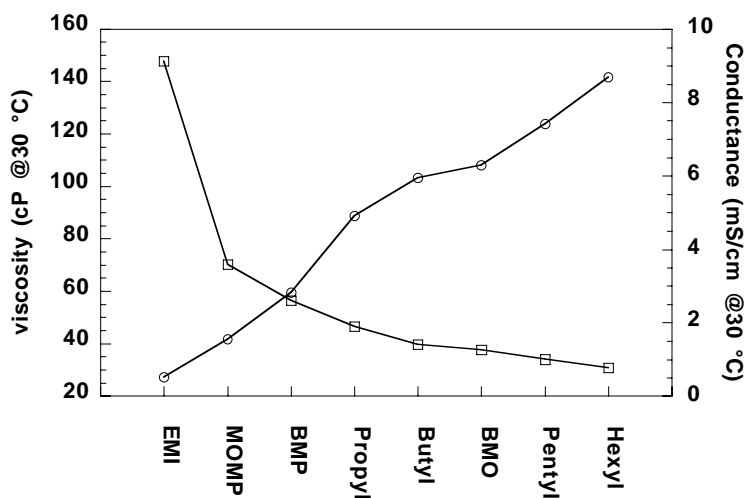


Figure 1. Viscosity (○) and conductivity (◻) of NTf₂ based ionic liquid salts as a function of cation.

Electrochemical Properties

Cyclic voltammograms depicting the electrochemical solvent windows of [EMI]NTf₂ and [NMe₂(*i*-Pr)(*n*-Pr)]NTf₂ are compared in Figure 2. The data shown for [NMe₂(*i*-Pr)(*n*-Pr)]NTf₂ is typical of both cyclic and acyclic quaternary ammonium based ionic liquids. While the cathodic limit is reached for [EMI]NTf₂ just before -2.0 V, this limit is extended to *ca.* -3.1 V for the quaternary ammonium salts. The anodic limit, most likely defined by oxidation of the NTf₂ anion, is observed near 3.0 V. The slight variation in anodic limit between [EMI]⁺ and [NR₄]⁺ salts is a real effect and is attributed to differences in ion-pairing between NTf₂ and the respective cations. These data indicate an effective working electrochemical window for [NR₄]NTf₂ ionic liquids of just greater than 5.5 V.

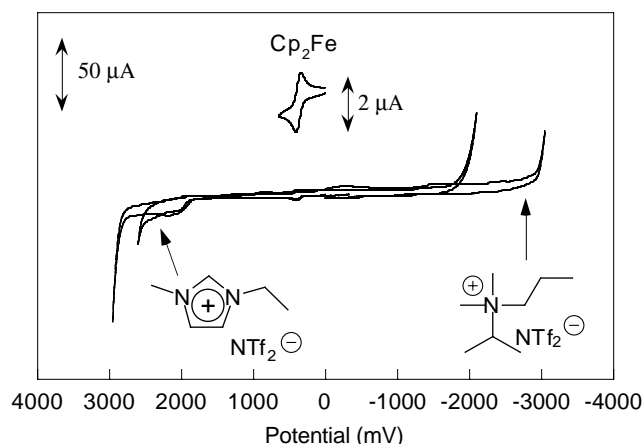


Figure 2. Cyclic voltammograms (CV) of $[EMI]NTf_2$ and $[NMe_2(i-Pr)(n-Pr)]NTf_2$ showing solvent limits at 25 °C (Pt working electrode, Ag/AgOTf reference electrode).

The cathodic boundary of $[NR_4]NTf_2$ salts have been further tested by examining the electrochemical behavior of highly electropositive sodium and potassium salts. For example, to a suspension of KH in the ionic liquid was added HNTf₂, which rapidly evolves hydrogen and forms a homogeneous solution of KNTf₂. A cyclic voltammogram of this solution is shown in Figure 3. Sweeping the potential negative gives a rapid rise in current at *ca.* -3.0 V due to plating of potassium metal on the cathode. Reversal of the potential sweep gives a distinctive stripping wave as electrodeposited potassium metal is oxidized from the platinum working electrode. A similar cyclic voltammogram was recorded for NaNTf₂ in which plating is observed at *ca.* -2.5 V.

To put this observation into perspective, the standard reduction potentials (aqueous) calculated for Na^+/Na^0 and K^+/K^0 are -2.714 and -2.924 V, respectively. The standard reduction potential calculated for Pu^{3+}/Pu^0 , the most technologically important actinide element, is only -2.07 V. In fact all of the standard reduction potentials calculated for the An^{3+} ions are less negative than Na^+/Na^0 . This analysis suggests that from a thermodynamic perspective, the electroplating of f-element ions should be readily achieved in these ionic liquid solvents. However, the actual coordination chemistry of the f-element ions dissolved in RTILs should play a fundamental role in the electroreduction process. Strongly coordinated counter ions such as chloride may kinetically inhibit the multi-electron reduction reaction, causing a distinctive over potential. In the following section, the potential coordination chemistry of simple, formally "bare" metal ions, dissolved in NTf₂ based ionic liquids is considered.

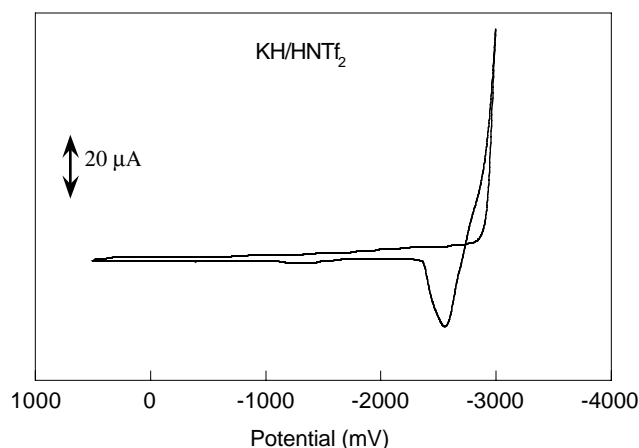
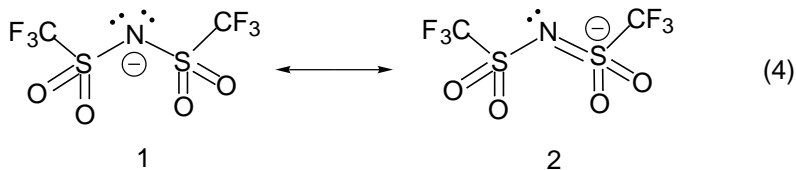


Figure 3. Electroplating and stripping of KNTf_2 dissolved in $[\text{NMe}_2(i\text{-Pr})(n\text{-Pr})]\text{NTf}_2$ (Pt working electrode, Ag/AgOTf reference electrode).

Structure and Coordination Chemistry of NTf_2 Based Ionic Liquids

The coordination chemistry anticipated for the ionic liquids under investigation in this work are related to the electronic structure of NTf_2 . Single crystal X-ray diffraction experiments carried out for $[\text{NMe}_3(i\text{-Pr})]\text{NTf}_2$ (mp = 150°C) reveal short S–O and N–S bond lengths most consistent with resonance structure **2** (eq 4). Golding and coworkers recently reported the structure of



$[\text{1,2,3-benzylmethylethylimidazolium}]\text{NTf}_2$ and reached a similar conclusion (8). Delocalization of negative charge within the S–N–S core can account for the weak coulombic attraction between the NTf_2 anion and weakly Lewis acidic organic cations (*i.e.* low lattice energy and low melting points).

Although little interaction between NTf_2 and weak Lewis acids is indicated by structural studies of organic NTf_2 salts, the potential of bonding interaction with Lewis acidic metal ions should be considered. Only one crystal structure of an NTf_2 anion coordinated to a metal atom has been reported. In this case, metrical data obtained for $\text{Cu}(\text{CO})_2(\text{NTf}_2)$ demonstrates that the S–N–S unit

becomes slightly modified upon coordination to the copper (I) atom (9). The S–N–S angle is found to become more acute in the complex (121.9°) compared to [NMe₃(*i*-Pr)]NTf₂ (124.5°). The S–N bond length also relaxes to *ca.* 1.630 Å compared to 1.575 Å in the uncoordinated anion. These data indicate that resonance structure **1** becomes comparably more important in the metal complex. In this study the donor ability of ⁻NTf₂ was determined to be weaker than the triflate anion, ⁻OSO₂CF₃, but stronger than [AsF₆]⁻ through comparison of the ν(CO) stretching frequencies measured for Cu(CO)₂X (X = ⁻OSO₂CF₃, ⁻NTf₂, and [AsF₆]⁻). These data suggest that ⁻NTf₂ based ionic liquids will behave as moderate donor solvents.

In order to obtain a better measure of coordinating ability of ⁻NTf₂ based ionic liquids, we have recently developed a simple spectroscopic probe to estimate the solvent Gutmann Donor Number (DN) (10). The benzylic ¹⁹F NMR chemical shift of perfluorobenzyl iodide [ICF₂(C₆F₅)] is found to be linearly dependent upon the DN of the solvent in which the probe is dissolved. By subsequently measuring the benzylic ¹⁹F NMR chemical shift in representative ⁻NTf₂ based ionic liquids, the DN of these solvents can be estimated at *ca.* 10±1 (11). A DN of 10 is analogous to the coordinating ability of benzonitrile (NCPh). These ionic liquids should be more strongly coordinating than solvents such as nitromethane (DN = 2.7) or chloroform (DN = 4), but will be weaker donor solvents than acetonitrile (DN = 14.1) or acetone (DN = 17) (12). The coordination chemistry and electrochemical behavior of lanthanide and actinide metal ions dissolved in the [NR₄]⁺NTf₂⁻ ionic liquids summarized in this chapter are the subject of continued investigation.

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